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ION-EXCHANGE MEMBRANES

-USSR-

By V. S. Titov

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ION-EXCHANGE MEMBRANES

-USER-

[Following is the translation of an article by V.S. Titor entitled "Ion-Exchange Membranes -- The Application of Ion-Exchange Membranes in Chemical Technology" [see note] in Plasticheskiye Massy (Plastics), No 1, Moscow, January 1960, pages 55-59.]

Ion-exchange membranes are electrochemically active plastic sheets capable of producing ion-exchange effects. These two main properties determine the basic areas of technological utility of the membranes; they are used as ion exchangers or as electrochemically active partitions (diaphragms) in electrolytic apparatus.

The uses of the membranes as ion-exchangers are at present limited. This is explained by the fact that the standard industrially-produced membranes are mainly of the heterogeneous type whose ion-exchange capability is lower than that of the corresponding ion-exchange resins; the reason for this lies in the presence of an inert (with reference to ion-exchange properties) high-polymer binder in the membrane material. In a number of cases it is nevertheless more expedient to employ ion-exchange membranes.

Thus, for example, the cation-exchange membrane of the sulphuric-acid type saturated with lead and other heavy-metal ions can serve as a convenient shielding material for certain types of radiation. Sheets of ion-exchange material saturated with radioactive isotopes can be used as a radiation source, for example, in medical and laboratory prac-

[Note: Theory, Production Methods, Properties -- see Plasticheskiye Massy (Plastics), No 3, 1959.]

tice as pliable applicators for local irradiation.

Ion-exchange processes in the technology of solvent demineralization can in many cases be significantly modernized if ion-exchange resins are replaced by endless ribbons of ion-exchange membrane material. This concept allows the ion-exchange process to be placed on a continuous basis with full automation.

Figure 1 shows one of the possible schematic patterns featuring ion-exchange membranes in the form of continuous ribbons.

Unwinding from roll 1, the cation-exchange ribbon passes through a recharger solution in basin 2, then through the working solution in basin 3 and back on roll 1.

The anion-exchange ribbon unwinds from roll 5, passes through the recharger solution in basin 4, into the working solution in basin 3, and then rewinds onto roll 5.

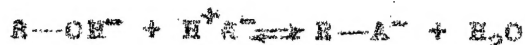
The motion of the ribbons can be parallel and oppositely-directed. Several ribbons can be made to pass through the working solution instead of just one pair.

Thus, if the working basin contains a water solution to be freed of a given salt K^+A^- , then the passage through it of a cation- and anion-exchanger pair of ribbons yields a simultaneous cationization and anionization process:

On the cation-exchange ribbon we have:



And on the anion-exchange ribbon:



The most extensive and promising area of ion-exchange membrane application, however, lies in their use as active partitions for electrolyte baths in electrochemical processes, which are in the main of the electrodialytic type.

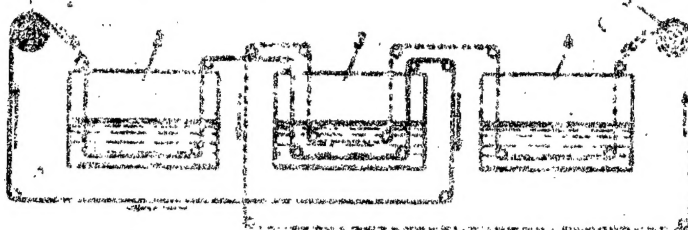


Figure 1. A schematic diagram for the demineralization of solutions with the aid of ion-exchange ribbons.

As is known, electrodialysis is a complex process involving a combination of electrolytic, dialytic, and electro-osmotic phenomena. The studies of O.N. Grigorov et al. (project supervisor -- I.I. Zhukov) (1) served to indicate that the character of this process is basically determined by the properties of the diaphragmatic partitions which close off the solution in the central compartment from the electrode areas. The use of ion-exchange membranes in place of porous diaphragms in this process to a considerable extent alters the quantitative and qualitative character of the process, since the basic process producing electrodialysis is the passage of ions in an electric field through the membrane serving as the partition, and which has a specific effect on ion passage.

The foregoing can be illustrated by the following example: Let us imagine an electrodialytic pattern for an Na_2SO_4 solution using electrochemically inactive diaphragms (Figure 2). In this case, a considerable portion of the electrical energy will be expended on the useless transference of H^+ and OH^- ions from the electrode compartments into the central section; the current efficiency for the system will amount to approximately 18%.

If now the inactive diaphragms were to be replaced by ideal ionically semipermeable membranes, namely an anionically permeable membrane on the anode side and a cationically permeable one on the cathode side (Figure 3), then there will be no transference of H^+ and OH^- ions from the electrode areas into the central compartment; thus, no additional electrical energy will have to be expended and the current efficiency of the system in the ideal case will constitute 100%. Under actual conditions, ion-exchange membranes assure a current efficiency of nearly 90-95% for the given process.

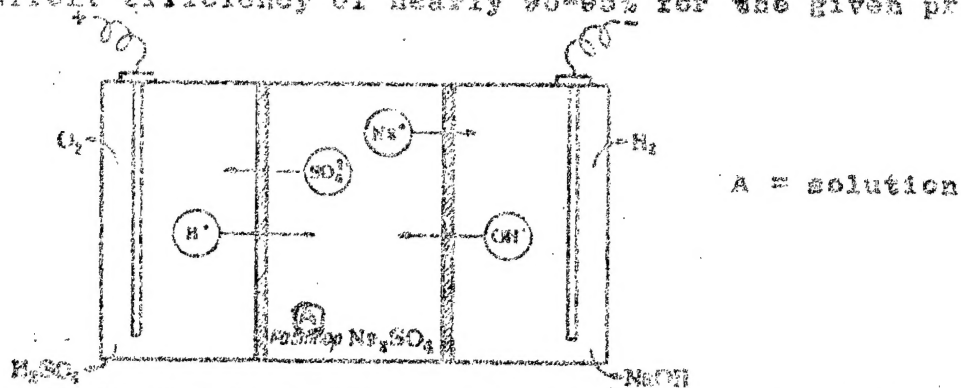


Figure 2. A schematic diagram for the electrodialysis of an Na_2SO_4 solution with the aid of inactive diaphragms

In addition, the reverse diffusion of Na^+ and SO_4^{--} ions out of the electrode areas into the central compartment which occurs in the case of porous membranes is actually reduced to a minimum when ion-exchange membranes are used, as a result of the high density of the latter.

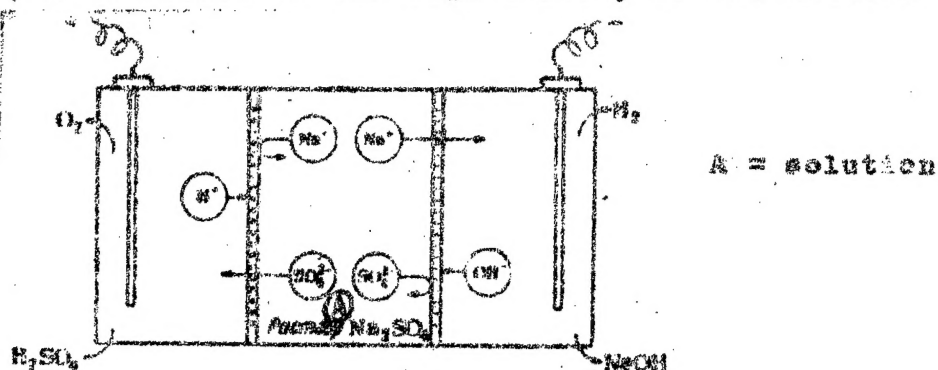


Figure 3. A schematic diagram for the electrodialysis of an Na_2SO_4 solution with the aid of ion-exchange diaphragms.

It may be seen from this example that the effectiveness of electrodialytic processes may be increased considerably through the use of ion-exchange membranes; this fact is of great theoretical and practical significance.

Obviously, the effectiveness of using ion-exchange membranes will in the last analysis be evaluated with reference to electrical energy expenditures.

The concept of current consumption in the electrodialytic process may be aptly rendered through the introduction of a notion of apparent current efficiency which is defined as the ratio of theoretically required energy consumption (according to Faraday's law) to the actual amount of electrical energy expended:

$$\eta = \frac{(C_H - C_L) \cdot V \cdot 96500}{It}$$

where C_H and C_L are the initial and final electrolyte concentrations in the middle compartment;

V is the volume of the compartment;

" It " is the amount of electricity.

The theoretical efficiency (in %) according to current with the use of ion-exchange membranes may be calculated by means of the equations suggested by A.V. Markovich

for porous diaphragms (1):

$$\eta \text{ for cation} = 100 (t_K^+ - t_A^+)$$

$$\eta \text{ for anion} = 100 (t_A^- - t_K^-)$$

where t_K^+ and t_A^+ are the cation transfer numbers for the pores of the cathode and anode diaphragms;
 t_K^- and t_A^- are the anion transfer numbers.

If current efficiency depends to a significant degree on membrane selectivity, then the expenditure of electrical energy is considerably affected by the electrical resistivity of the membranes.

Electrical energy consumption may be calculated by means of the following formula:

$$\omega = \frac{\left(E_{el} + \frac{\sum \delta \rho_i}{S} \right) It}{\eta}$$

where $E_{el} + \frac{\sum \delta \rho_i}{S}$ is the total voltage on the solution consisting of electrode loss $E_{el} \approx 2$ volts and ohm losses in the electrolyte and membranes, $\frac{\sum \delta \rho_i}{S}$;

δ, S, ρ are, respectively, the thickness, area and electrical resistivity of the membranes;

"It" is the amount of electricity;

η is the coefficient of current efficiency (efficiency according to current).

In planning electrodialytic processes employing ion-exchange membranes, as well as in general technological practice, it is necessary to take into account the electro-osmotic water transference phenomenon. In most technological situations involving the use of membranes, this effect is undesirable. This is easily seen for the case of electrodialysis in a three-compartment cell as shown in the schematic diagram of Figure 3. Ionic diffusion from the central compartment into the electrode areas under the action of electric current lowers the salt concentration in the middle section. Simultaneously, the electro-osmotic transference of water is proceeding in the same direction, i.e., from the central section into the electrode compartments, thus tend-

ing to increase salt concentration in the central section.

In addition to the purely electro-osmotic transference of water from the central compartment into the electrode areas, water is also carried along by the moving ions in the form of water jackets. The amount of water transported by electro-osmosis depends on the concentration of the external solution (water transference increases with reduced concentration), the nature of the moving ions, current density, physical and physico-chemical properties of the membranes, and other factors.

Electrochemical processes using ion-exchange membranes are performed in apparatus (electrolytic baths) of various design. The simplest type is a two-compartment cell, i.e., cathode and anode areas separated by a membrane. In such a cell it is possible, for example, to obtain a free acid from one of its salts. If a cation-exchange membrane is used as the partition, the salt solution passes into the anode compartment. This is the method used at the present time for obtaining sebacic acid from sodium sebacinate. The sodium ions migrate from the anode area into the cathode compartment, and the free sebacic acid precipitates in the form of a soft, white precipitate as the acidity of the anolyte increases; an alkali forms in the cathode compartment. The advantage of this method of obtaining sebacic acid consists in the fact that there is no need to add sulfuric acid to the sodium sebacinate, the product is not contaminated by sodium sulfate; another advantage is that a useful base is also produced in the process.

The derivation of free amines from their salts, such as ethylenediamine, through the use of an anion-exchange membrane as partition has also been described.

In the simultaneous utilization of cation- and anion-exchange membranes, the electrolytic cell is divided into three sections; as was described above. The solution to undergo dialysis is placed in the central compartment. This is the most extensively-used type of electrolytic cell.

Finally, it is possible to use electrolytic baths with a large number of alternating cation- and anion-exchange membranes (Figure 4).

Multi-compartment electrodialyzers are presently being used in the freshening of salt water (including sea and ocean water).

The essential process in the electrochemical method of water freshening is a multi-compartment cell with

exchange membranes is as follows. In a multi-compartment electrodialyzer with two electrodes, the cation- and anion-exchange membranes are placed in an alternating configuration. The first cation-exchange membrane is placed next to the cathode, while the anion membrane -- the last in the series -- goes next to anode, as may be seen from Figure 4.

As a result of the fact that membranes are characterized by the property of ionic semipermeability, the passage of current through such a cell will freshen water in some compartments, while in others, salt concentration will increase.

The freshened water and concentrated salt solution are drawn out of the cell through different outlets. The water to be freshened may be supplied to such a multi-compartment cell simultaneously (parallel in-flow) as is shown in Figure 4. The successive passage of the solution through each compartment is also possible.

Some of the ions in the water undergoing purification are neutralized at the appropriate electrodes; the corresponding electrode reaction products accumulate and must either be drawn off continuously or periodically cleared away. In the electrodialysis of salt water, the main products of electrode reactions at the cathode are hydrogen and a base; the products formed at the anode are oxygen, chlorine, and acid.

The problem of salt-water freshening is of enormous significance to the national economy. In many regions of the Soviet Union there is a severe shortage of fresh water both for technological purposes and for human and animal consumption. Also very important is the problem of supplying seagoing vessels with fresh water.

At the basis of the old methods for obtaining fresh water, and which are still extensively used today, was evaporation.

The electrochemical method of salt-water freshening, known since the beginning of the 20th century, had not been introduced into industry due to its low efficiency (about 20%). With the advent of ion-exchange membranes, however, the situation changed.

Comparing the economy of various methods of salt-water freshening (ordinary evaporation, multi-phase evaporation, vacuum evaporation, thermocompressive distillation, the ion-exchange method, and the electrical membrane method), foreign authors (2,3) concluded that the last of these is

the most economical. This method of freshening has several distinct advantages: it is highly efficient and can be easily automated without requiring large-scale equipment and numerous operational personnel.

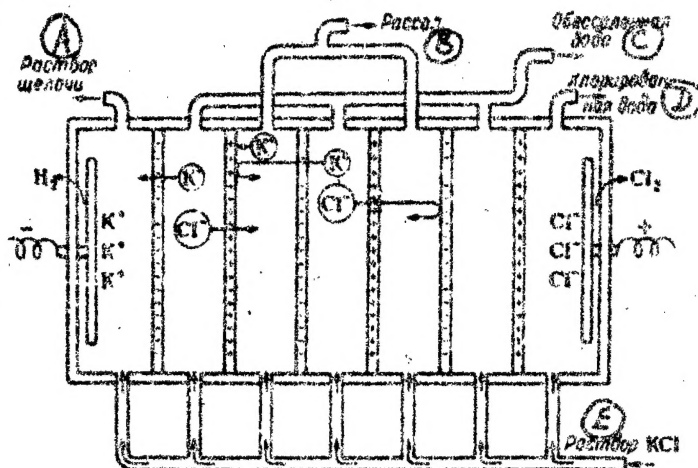


Figure 4. A schematic diagram for a multi-compartment electrodialyzer.

- A = Alkaline solution.
- B = Salt solution.
- C = Salt-free water.
- D = Chlorinated water.
- E = KCl solution.

It should be mentioned, however, that the electrical membrane method of salt water freshening is not universally applicable.

Numerous studies on the electrochemical freshening of salt water with the aid of ion-exchange membranes (2-17) provide some basis for the conclusion that this method is most profitable in desalinating water with a salt content of 2-10 grams/liter down to a concentration of 300-500 milligrams/liter. In freshening water with a 10-30 gram/liter salt content (sea and ocean water), other methods can compete successfully with the electrical ion-exchange membrane process. Finally, it is considered unprofitable to employ this technique in freshening water containing over 30 grams of salt per liter.

It is also not expedient to perform deep desalination down to a salt concentration of 100 milligrams/liter, since in this case energy expenditures rise considerably.

One of the first semi-industrial installations of

this type was the 30-compartment electrical ion-exchange membrane apparatus with a yield of 370.5 liter/hour built in Holland (9), which freshened sea water down to a salt content of 300 milligrams/liter.

At the present time, the industrial production of electrical water-freshening installations making use of ion-exchange membranes has been mastered by the firm of Ionics (USA).

One of the foreign references (17) provides basic technical and economic data regarding the industrial installations built by Ionics, and operating in Texas, Arizona, South Dakota, Bahrain Island, etc. (see Table).

Laboratory studies on the freshening of sea water by the electrical ion-exchange membrane method were conducted in the USSR during 1953-1958 (18). These investigations continued under semi-industrial conditions during 1957-1958 (19).

Early in 1953, the first domestic electrical membrane water-freshening installation with yield of 15 cubic meters per 24-hour period was assembled on the Black Sea vessel "Tula".

Studies of the electrical ion-exchange membrane method of water freshening have as their basic purpose the achievement of maximum economy.

Wigner and others (18,19) conducted theoretical and practical research on the water-freshening process in multi-compartment cell. They determined the dependence of the productivity of a multi-compartment installation on electrical energy expenditure, and current efficiency on the basic electrochemical characteristics of membranes.

It may be considered as having been established that the net electrical energy expenditure may be lowered if:

- 1) the membranes employed are of minimum electrical resistivity and maximum selectivity;
- 2) a maximum number of membranes (cell compartments) is used, while the distance between each pair of membranes is kept to a minimum;
- 3) the reverse diffusion of ions and electro-osmotic water transferences are kept to a minimum.

Experience in the operation of installations abroad shows that the net expenditure of electrical energy for freshening water down to a salt concentration of 300-500 milligrams/liter is equal to: 40 kWh/m^3 (kilowatt-hours/meter³) for ocean water (32 grams/liter), about 50 kWh/m^3 for sea water

Technical-Economic Data on the Industrial Electrical Ion-Exchange Membrane Installations Built by the Firm of Ionice

Location	Date operations initiated	Type of water freshened	Salt content in brine/liter		Output in liters/hour	Membr. surface m ²	Electr. energy expend. Kw-h/m ³
			initial	final			
US West Coast	Feb. 1954	Ocean	32	0.3	65	9.3	26.5
"	July 1954	Well	2.4	1.0	380	7	0.53
"	Oct. 1954	"	2.0	0.3	760	11.5	0.39
Texas	"	"	1.7	0.4	4550	46	0.32
Arizona	Jan. 1955	"	4	0.4	3785	70	0.53
South Dakota	Aug. 1955	"	2	0.7	6435	--	0.26
Bahrain Is.	1955	"	3.15	0.4	4770	87	0.42
California	Sep. 1955	"	3.5	0.17	285	10	0.39
Radar station on US East Coast	Nov. 1955	Ocean	32	0.5	335	35	39.6

(18 grams/liter), about 10 kw-h/m³ for water of medium salinity (7-10 grams/liter), and about 0.5 kw-h/m³ for water of low salinity (2-4 grams/liter).

It is commonly held that with an installation capable of producing 1 cubic meter of fresh water per hour, the membrane surfaces for freshening slightly saline water should be 25 m² (meters²); the surfaces should be 100 m² for sea water, and 170 m² for ocean water.

A reasonable cost scale for turning out fresh water in the USSR is considered to be as follows: 15-30 cents for 1 m³ of ocean and sea water, and 2-5 cents for 1 m³ of slightly saline water.

In addition to salt-water freshening, other areas of membrane application are described in the literature. For example, it has been proposed that membranes be used as electrodes, as well as for determining the activity of various ions (20-22). Manecke (23) has suggested the construction of a membrane accumulator consisting of transversely positioned cation-exchange and anion-exchange membranes, while Fattle (24) proposed a membrane generator for producing electrical energy based on the principle of utilizing the energy released in the mixing of sea water with fresh water.

There are descriptions of methods for removing minerals from organic materials (25,26), concentrating radioactive waste waters (27), separation and identification of various alkaloids (28), and the derivation of pure sodium hydroxide and hydrochloric acid (29). An original method for obtaining sodium hydroxide with a low chloride content was devised by Krishtalik (30).

Detailed descriptions of methods for reclaiming iron and sulfuric acid from etching solutions (31) have been published. The possibility of removing mineral impurities from sugar and hydrolyzed syrups has been suggested.

High-voltage electrodialysis has been used for purifying silicon oxide, titanium oxide, and other valuable materials. The latter method holds great promise in the field of semi-conductor material production.

A number of suggestions concern the use of membranes in the absence of electric current and with the utilization of purely osmotic processes. Thus, for example, the possibility of separating electrolytic mixtures such as NaOH and NaCl by osmotic means has been proposed (32).

In our opinion, the latter process could conceivably be

carried out in a multi-compartment cell having ion-exchange membranes as partitions (Figure 5). The NaOH solution containing an admixture of NaCl is introduced into compartments 1, 3, and 5. Compartments 2 and 4 are filled with distilled water.

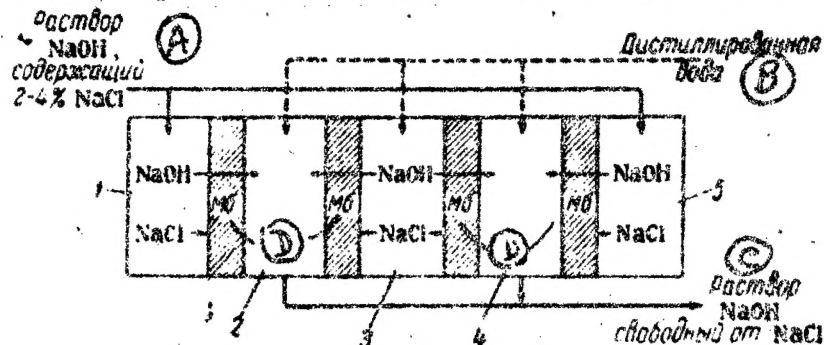


Figure 5. A schematic diagram for the osmotic removal of NaCl admixture from NaOH solution with the aid of ion-exchange membranes. Numbers of 1-5 indicate compartments. A = NaOH solution containing 2-4% NaCl. B = Distilled water. C = NaOH solution free from NaCl. D = Membranes.

Both electrolytes in compartments 1, 3, and 5 will diffuse into sections 2 and 4; due to the great difference in the concentrations of the electrolytes in the additional solution, however, compartments 2 and 4 will be filled mainly with NaOH free from chlorides. The purified NaOH solution is then drawn off.

This principle may also be used for obtaining fresh water from sea and ocean water, as well as for obtaining various purified substances (both mineral and organic).

Ion-exchange membranes are a new plastic material. They are not being extensively used as yet, but even at this stage it may be confidently asserted that in the future the applications for these materials will be both varied and numerous.

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